EVALUATION OF THE INTERACTIVE CHEMISTRY OF COAL-PETROLEUM SYSTEMS USING MODEL AND ACTUAL REACTANTS

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The coprocessing of coal with petroleum residuum simultaneously liquefies coal and upgrades petroleum residuum into higher value products. However, coal and petroleum residuum manifest very different chemical properties with coal being more aromatic with a H/C ratio of 0.6 - 0.8 and petroleum residuum more aliphatic with a H/C ratio of 1.4 to 1.6. Although a number of studies have demonstrated the feasibility of coprocessing on the basis of product selectivity and metals reduction (1-8), the interactive chemistry involved between the coal and petroleum materials during coprocessing has not yet been determined.

In this study, the interactive chemistry between coal and petroleum molecules has been examined: first by using model compound types representative of coal and residuum and then by combining the model systems with Illinois No. 6 coal and Maya topped long residuum (TLR). The model systems, composed of naphthalene (NAPH) representing aromatics, 1,4-dimethylcyclohexane (DMC) representing saturated compounds, phenol (PN) representing phenolics, benzothiophene (BZT) representing sulfur compounds, and quinoline (QN) representing nitrogen compounds, were reacted thermally and catalytically using a Shell 324 $NiMo/Al_2O_3$ catalyst. The model systems were reacted individually and then combined together to ascertain the effect of the different components on the thermal and catalytic reactions of the different model systems. Illinois No. 6 coal and Maya TLR were each, respectively, added to the model compound systems and reacted thermally and catalytically.

Experimental

Model Reactions. The model systems, NAPH, DMC, PN, BZT and QN, were reacted as 2 wt% reactant in hexadecane at 350°C with 1250 psi H_2 (cold) for 30 minutes and agitated at 850 rpm. The reactor used was a ~12.3 cc stainless steel vertical tubing bomb with a Nupro fine metering valve for gas introduction. For the catalytic reactions, 0.25 g of presulfided 1/32" Shell 324 $NiMo/Al_2O_3$ extrudates were used. The reaction systems were built in the following manner: NAPH; NAPH and DMC; NAPH, DMC and PN; NAPH, DMC and BZT; and NAPH, DMC and QN. A Varian Model 3700 FID gas chromatograph equipped with a 30 m DB-5 fused silica column was used for analyzing the products from model systems reactions. Para-xylene was used as an internal standard. Product identification was achieved by spiking with authentic compounds and by GC/MS analysis. Gases produced during the reaction were analyzed for hydrogen using a Varian 3700 TCD chromatograph.

Coal and Residuum Reactions. Illinois No. 6 coal (-15 mesh) and Maya TLR were each added individually at 10 wt% to the model compound systems and were reacted under the thermal and catalytic conditions described above. Typical analyses of Illinois No. 6 coal and Maya TLR are detailed elsewhere (5). When residuum was reacted with the model systems, insoluble matter (IM) was produced during the reaction. The IM was recovered by precipitating it from the product mixture by centrifuging and decanting the liquid product mixture. The IM produced during thermal residuum - model systems reactions averaged 8% while that produced during catalytic reactions averaged 5%.

Results and Discussion

In this investigation, each model system produced a number of products from the catalytic reactions. In order to summarize and compare the data, several terms have been defined. These terms are: percent hydrogenation, percent deoxygenation, percent desulfurization, percent denitrogenation, and percent hydrogenolysis. Percent hydrogenation is the number of moles of hydrogen required to produce the observed product distribution from a given reactant as a percentage of the moles of hydrogen required to obtain the most hydrogenated product. Percent deoxygenation is the summation of the mole percents of components not containing oxygen. Percent desulfurization is the summation of the mole percents of the components not containing sulfur. Percent denitrogenation is the summation of the mole percent of the components not containing nitrogen. Percent hydrogenolysis is the mole percents of the components which have undergone cleavage of the carbon-heteroatom bond.

Naphthalene Hydrogenation. NAPH hydrogenation may be represented as a sequential and reversible reaction of NAPH hydrogenating to tetralin followed by hydrogenation to decalin. Thermal reactions of NAPH individually and in combination with other model systems showed no NAPH hydrogenation. Neither the addition of coal nor residuum affected the thermal hydrogenation of NAPH.

Significant hydrogenation of NAPH occurred under catalytic conditions as shown in Table 1. The addition of DMC had no influence on NAPH hydrogenation; however, the addition of the heteroatomic species, PN, BZT, and QN, reduced NAPH hydrogenation with QN giving the most substantial reduction. The addition of Maya TLR and coal to NAPH each produced a substantial reduction in NAPH hydrogenation with residuum being more detrimental than coal under these process conditions. It should be noted that at 350°C not all of the coal was converted to soluble products, thereby reducing its influence on NAPH hydrogenation. Addition of DMC and the heteroatomic species to either the NAPH/Maya TLR or NAPH/coal systems further reduced the hydrogenation of NAPH with the order of influence being QN > BZT > PN > DMC. In terms of being most detrimental to NAPH hydrogenation, the order of model components ranked as QN > BZT > PN > DMC and of coal and residuum ranked as Maya TLR > Coal.

Table 1
Effect of Different Systems on the Catalytic
Hydrotreatment of Naphthalene

Systems	Hydrogenation,%
Naphthalene	94.7
Naphthalene/DMC	94.8
Naphthalene/DMC/Phenol	89.0
Naphthalene/DMC/Benzothiophene	75.9
Naphthalene/DMC/Quinoline	32.5
Naphthalene/Coal	57.8
Naphthalene/Resid	39.4
Naphthalene/DMC/Coal	57.0
Naphthalene/DMC/Resid	36.1
Naphthalene/DMC/Phenol/Coal	54.3
Naphthalene/DMC/Phenol/Resid	36.4
Naphthalene/DMC/Benzothiophene/Coal	50.6
Naphthalene/DMC/Benzothiophene/Resid	32.1
Naphthalene/DMC/Quinoline/Coal	17.9
Naphthalene/DMC/Quinoline/Resid	16.3

Phenol Hydrodeoxygenation. PN undergoes deoxygenation to form benzene and further hydrogenation to cyclohexane under hydrogenation conditions. The benzene - cyclohexane reaction is reversible (9). Under thermal conditions, no conversion of phenol was observed. Under catalytic conditions, PN underwent complete hydrogenation and deoxygenation as shown in Table 2. Neither the addition of NAPH and DMC nor coal had any effect on the hydrogenation or deoxygenation of PN. However, the addition of Maya TLR reduced both PN hydrogenation and deoxygenation. The addition of NAPH and DMC to the PN/Maya TLR system moderated the detrimental effect of the residuum.

Table 2
Effect of Different Systems on the
Catalytic Hydrotreatment of Phenol

Systems	Hydrogenation,%	Deoxygenation,%
Phenol	100	100
Phenol/DMC/Naphthalene	100	100
Phenol/Coal	100	100
Phenol/Resid	82.0	82.0
Phenol/DMC/Naphthalene/Coal	100	100
Phenol/DMC/Naphthalene/Resid	88.9	88.9

Benzothiophene Hydrodesulfurization. BZT undergoes hydrogenation to 2,3-dihydrobenzothiophene followed by hydrogenolysis to o-ethylphenol, then hydrogenolysis to ethylbenzene and, finally, hydrogenation to ethylcyclohexane (10). No reaction was observed with BZT under thermal reaction conditions. Under catalytic conditions, two products, ethylbenzene and ethylcyclohexane, were formed in agreement with the literature (9). For the individual BZT catalytic reaction as presented in Table 3, complete desulfurization and ~71% hydrogenation occurred. The addition of the hydrocarbons, NAPH and DMC, as well as coal and Maya TLR reduced the hydrogenation of BZT. In contrast, the residuum only reduced the desulfurization and hydrogenolysis of BZT. The addition of NAPH and DMC to the BZT/Maya TLR system moderated the effect of the residuum by increasing the percent hydrogenation by 3% and both desulfurization and hydrogenolysis to 100%.

Table 3
Effect of Different Systems on the
Catalytic Hydrotreatment of Benzothiophene

Systems	Hydrogenation,%	Desulfurization,%	Hydrogenolysis,%
Benzothiophene	71.2	100	100
Benzothiophene/ DMC/Naphthalene	66.3	100	100
Benzothiophene/ Coal	56.3	100	100
Benzothiophene/ Resid	48.6	96.2	96.2
Benzothiophene/ DMC/Naphthalene/ Coal	55.4	100	100
Benzothiophene/ DMC/Naphthalene/ Resid	51.6	100	100

Quinoline Hydrodenitrogenation. The hydrodenitrogenation of quinoline follows a complicated pathway (11) as shown in Figure 1. In thermal reactions at 350°C, 13% THQ was produced. Neither hydrogenolysis nor denitrogenation was observed. Introduction of NAPH and DMC decreased QN conversion and reduced the amount of THQ produced by half. The addition of coal to the thermal QN reaction blocked conversion of QN to THQ. The addition of NAPH and DMC to the QN/coal system had no effect. The thermal reaction of Maya TLR with QN also prevented any hydrogenation of QN; the addition of NAPH and DMC to the Maya TLR/QN system had no effect.

In the catalytic QN reaction as shown in Table 4, substantial hydrogenation, 79.4%, denitrogenation, 48.9%, and hydrogenolysis, ~50.6%, occurred. The addition of NAPH and DMC to QN increased both denitrogenation, 54.6%, and hydrogenolysis, 56.6%. Both the addition of coal and residuum to QN substantially reduced hydrogenation, denitrogenation and hydrogenolysis. The addition of NAPH and DMC to the QN/coal moderated slightly the effect of coal on denitrogenation and hydrogenolysis. The addition of NAPH and DMC to the QN/resid system increased all three reactions, hydrogenation, denitrogenation and hydrogenolysis, more substantively than the QN/coal system.

Table 4
Effect of Different Systems on the Catalytic Hydrotreatment of Quinoline

Systems	Hydrogenation,%	Denitrogenation,%	Hydrogenolysis,%
Quinoline	79.4	48.9	50.6
Quinoline/DMC/ Naphthalene	79.9	54.6	56.6
Quinoline/Coal	61.0	35.1	39.3
Quinoline/Resid	60.6	34.7	42.5
Quinoline/DMC/ Naphthalene/Coal	61.1	36.6	41.0
Quinoline/DMC/ Naphthalene/Resid	62.8	38.0	47.0

Summary

Thermal hydrogenation reactions at 350°C as performed in this work did not lead to the hydrogenation of any of the model systems except for QN. Combinations of the model systems did not result in thermal chemical reactions among the species except in the case of QN where the addition of hydrocarbons reduced the amount of hydrogenation while coal and residuum totally eliminated it.

In the catalytic reactions, no effect on the hydrogenation of NAPH was observed by the presence of DMC. However, the addition of NAPH and DMC to the reaction systems containing Maya TLR/PN, Maya TLR/BZT, and Maya TLR/QN showed a promoting effect on heteroatom removal (N,S, and O) and hydrogenation of BZT and QN under the catalytic conditions. In the coal system, the addition of NAPH and DMC promoted denitrogenation and hydrogenolysis of QN but did not effect the other reactions. In the QN reaction alone, the promoting effect by the presence of NAPH/DMC on the denitrogenation and hydrogenolysis of QN was observed but the hydrogenation of QN was not affected. The only inhibitor of PN hydrogenation and deoxygenation was Maya TLR whose effect was moderated by

the addition of NAPH and DMC. NAPH hydrogenation was inhibited by the addition of all heteroatomic species coal and residuum, with QN and Maya TLR being the most detrimental.

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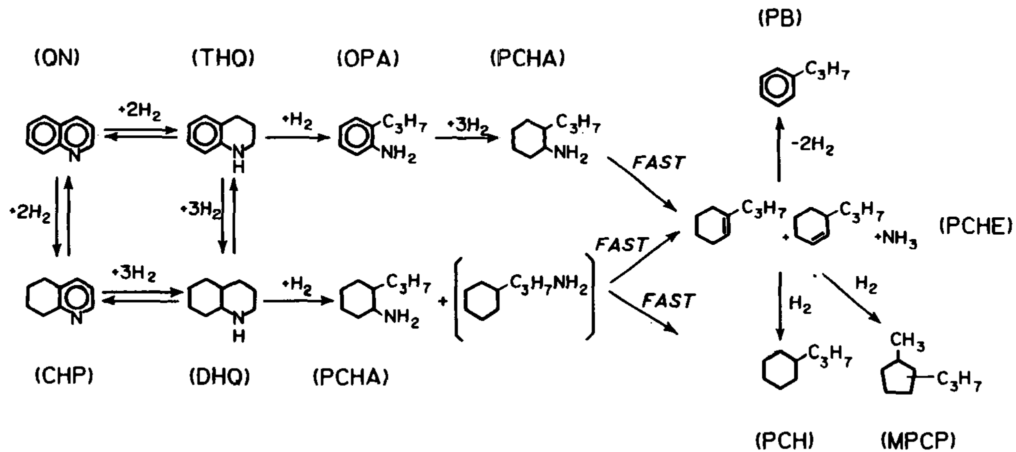
Figure 1. Reaction Pathway for Quinoline Hydronitrogenation



QN	– quinoline	PCHA	– propylcyclohexylamine
THQ	– 1,2,3,4 -tetrahydroquinoline	PB	– propylbenzene
CHP	– 2,3 - cyclohexenopyridine	PCHE	– propylcyclohexene (1,1 or 1,3)
DHQ	– *decahyroquinoline (cis and trans isomers)*	PCH	– propylcyclohexane
OPA	– o-propylaniline	MPCP	– methylpropylcyclopentane